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<p>(54) Title: A COMPOSITION COMPRISING A BLEND OF AN ETHYLENE POLYMER OR COPOLYMER WITH SORBITOL OR A SORBITOL DERIVATIVE</p>		
<p>(57) Abstract</p> <p>Films formed from blends of high impact LLDPE and sorbitol derivatives exhibit excellent optical properties, particularly excellent haze properties.</p>		

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A Composition comprising a Blend of an Ethylene Polymer  
or Copolymer with Sorbitol or a Sorbitol Derivative

The present invention relates to a composition comprising  
5 a blend of an ethylene polymer or copolymer with a sorbitol or  
a sorbitol derivative. The composition according to the  
invention is particularly useful as a film or an extrudate.

It is known to use nucleating agents to modify the  
crystalline structure of thermoplastic polymers and to increase  
10 the temperature of crystallization and rate of crystallization.  
The polymer compositions, while in the heat-plastified state,  
can be fabricated into various articles, such as fibre,  
filaments, films, tubes or the like, by extrusion or moulded by  
compression or injection or otherwise into moulded articles and  
15 then cooled to set up the shape and induce crystallization. By  
increasing the temperature of crystallization and by increasing  
the rate of crystallization, the cycle time can be reduced and  
production rates increased.

According to the present invention there is provided a  
20 composition comprising a blend of:

- (i) 99.95 to 98.5 weight percent of an ethylene polymer  
or an ethylene copolymer; and
- (ii) 0.05 to 1.5 weight percent of sorbitol or a sorbitol  
derivative;

25 wherein the ethylene polymer or copolymer exhibits a MFR  
( $I_2/I_1$ ) of 15 to less than 30,  $M_w/M_n$  of 2.5 to 3.5 and a haze  
value of greater than 7.

Advantageously, the sorbitol or sorbitol derivative  
comprises a sorbitol derivative which is an ether or an ester  
30 of sorbitol.

Sorbitol has an empirical formula of  $H_8(COH)_6$ . The sorbitol  
derivative can be a mono-, di-, tri-, tetra-, penta-, or hexa-  
substituted.

Advantageously also, the sorbitol derivative has an  
35 empirical formula  $H_8[(COH)_n[(CO)_2X]_m]$  in which m is 0, 1, 2 or 3,  
n is in the range 0 to 6, and  $2m+n$  is equal to 6; and wherein  
X is selected from the group consisting of:

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- (1) alkyl or aryl of 1 to 8 carbon atoms;
- (2)  $-C(O)R$ , wherein R is alkyl or aryl of 1 to 8 carbon atoms;
- (3) admixtures of (1) and (2).

5 Preferably wherein m is in the range 1 to 3. In one embodiment m is 2 or 3.

In one embodiment n is in the range 1 to 6.

The sorbitol derivative is most preferably bis(dimethylbenzylidene) sorbitol or dimethyl-dibenzylidene  
10 sorbitol.

Examples of other sorbitol derivatives which may be used include sorbitol dibenzylidene, sorbitol hexacetate, sorbitol hexanicotinate, sorbitol monobenzylidene, sorbitol pentanitrate; sorbitol tricarbonat; sorbitol tri(o-chlorobenzylidene).

15 Production of dibenzylidene sorbitol derivatives has been disclosed in US-A-4016118 and US-A-5135975; according to these references dibenzylidene sorbitol is produced by reacting one mole of sorbitol and two moles of benzaldehyde in the presence of an acid catalyst at an elevated temperature.

20 Advantageously the ethylene copolymer is used in the blend, and it comprises linear low density polyethylene which is a copolymer of ethylene and at least one alpha olefin containing 3 to 10 carbon atoms.

Preferably the alpha olefin is 1-hexene.

25 In one preferred embodiment the composition according to the invention comprises a film exhibiting a haze value measured by ASTM D-1003 of less than 7, preferably less than 5.

In another preferred embodiment the composition according to the invention comprises an extrudate exhibiting a haze value  
30 measured by ASTM D-1003 of less than 7, preferably less than 5.

The film or extrudate of the present invention has improved optical properties over conventional films or extrudates: for example, conventional LLDPE exhibit haze values which exceed 10.

In addition to exhibiting improved optical properties, for  
35 example clarity, determined as haze values and measured by ASTM D-1003, the film and extrudate of the invention exhibit both increased rates of crystallization and temperatures of

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crystallization.

Production of the extrudable compositions or blends of the invention can be undertaken by mixing the molten ethylene polymer or copolymer by convention procedures, such as by using  
5 a Brabender Mixer under an inert atmosphere. The sorbitol derivative can be used in amounts ranging from 0.05 to 1.5 weight percent of the resulting blend of the sorbitol derivative and the ethylene polymer or copolymer. Preferably, the sorbitol derivative is used in amounts ranging from 0.05 to 0.5 weight  
10 percent of the resulting blend of the sorbitol derivative and the polymer or copolymer; and most preferably, the sorbitol derivative is used in amounts ranging from 0.1 to 0.25 weight percent of the resulting blend of the sorbitol derivative and the ethylene polymer or copolymer.

15 The ethylene polymer or copolymer of the compositions of the invention are preferably formed by catalysis in the presence of catalysts comprising metallocenes of transition metals. These catalysts can produce high density, medium density and linear low density polyethylene (LLDPE); linear low density  
20 polyethylene comprises copolymers of ethylene and alpha olefins.

The composition of the invention can be extruded or injection molded into articles or extruded and blown into films. Films can be produced which are 0.5 to 5.0 mils (13 to 130 micron), preferably 0.5 to 2.0 mils (13 to 52 micron),  
25 thickness.

The polymeric component of the composition according to the invention will now be described. The preferred polymeric components include those linear low density products, described in WO-9414855.

30 The linear low density products are copolymers, produced with ethylene and one or more C<sub>3</sub>-C<sub>10</sub> alpha-olefins. The copolymers preferably contain at least 80 weight % ethylene units. The comonomers used in the present invention preferably contain 3 to 8 carbon atoms. Suitable alpha olefins include  
35 propylene, 1-butene, 1-pentene, 1-hexene, 1-4-methylpentene, 1-heptene and 1-octene. Preferably, the alpha-olefin is 1-butene, 1-hexene, and 1-octene. The most preferred alpha olefin is 1-

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hexene.

Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/1-butene copolymers, 5 ethylene/1-hexene copolymers, ethylene/4-methyl-1-pentene copolymers, ethylene/1-butene/1-hexene terpolymers, ethylene/propylene/1-hexene terpolymers and ethylene/propylene/1-butene terpolymers.

Hydrogen may be used as a chain transfer agent in the 10 polymerization reaction of the present invention. Any gas inert to the catalyst and reactants can also be present in the gas stream.

These products can be prepared in the presence of a catalyst described below, and preferably under either slurry or 15 fluid bed catalytic polymerization conditions described below.

When the catalyst described below is used the copolymer products contain 0.1 to 2 ppm of Zr. The product is granular and has an average particle size of 0.015-0.035 inches (0.38 to 0.89 mm), and a settled bulk density from 15 to 36 lb/ft<sup>3</sup> (240 20 to 577 kg/m<sup>3</sup>). The particles may have a spherical shape. The are low density products are characterized by a density as low as 0.902 g/cm<sup>3</sup>. For applications herein, the density is generally greater than 0.900 g/cm<sup>3</sup>, preferably greater than 0.910 g/cm<sup>3</sup>, more preferably ranging from 0.911 to 0.929 g/cm<sup>3</sup>, 25 and most preferably ranging from 0.915 to 0.922 g/cm<sup>3</sup>.

Significantly, the narrow molecular weight distribution, linear low density copolymers have been produced with MI of between 0.01 and 1 inclusive. The low density products of the invention exhibit a MI which can range from 0.01 to 5, 30 generally from 0.1 to 5, and preferably from 0.5 to 4, and most preferably 0.8 to 2.0. For blown film, the MI of the copolymers is preferably 0.5 to 1.5; and for cast film the MI is preferably from 2 to 4.

The low density products of the invention exhibit a melt 35 flow ratio (MFR) range of 15 to 30, preferably from 15 to 22. In preferred products, the MFR ranges from 15 to 18. MFR is the ratio  $I_{21}/I_2$  [wherein  $I_{21}$  is measured at 190°C in accordance with

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ASTM D-1238, Condition F and  $I_2$  is measured at 190°C in accordance with ASTM D-1238, Condition E].

Melting points of the copolymer products range from 95°C to 130°C. Furthermore, the hexane extractables content is very low, typically ranging from 0.3 to 1.0 wt.%. The  $M_w/M_n$  of these products ranges from 2.5 to 3.5;  $M_w$  is the weight average molecular weight and  $M_n$  is the number average molecular weight, each of which is calculated from molecular weight distribution measured by GPC (gel permeation chromatography).

10 The polymeric component of the composition according to the invention exhibits balanced tear strength, as measured by ASTM D1922, which ranges from 50 to 600, preferably from 220 to 420 for machine direction and from 200 to 700, preferably from 200 to 600 for the transverse direction. They also give high modulus, as measured by ASTM D882 which ranges from  $1.0 \times 10^4$  to  $6.0 \times 10^4$  psi (717 KPa), preferably from  $1.8$  to  $4.5 \times 10^4$  psi (717 KPa); high tensile yield, as measured by ASTM D882 which ranges from  $0.7$  to  $3.0 \times 10^3$  psi (710 KPa), preferably from  $1.5$  to  $2.3 \times 10^3$  psi (710 KPa).

20 Films made of the polymeric component of the composition according to the invention exhibit excellent optical qualities as determined by haze studies, measured by ASTM D-1003 which means that haze is generally between 7 to 20. Films of inferior haze properties exhibit a haze of greater than 10. The importance of the optical properties of LLDPE depend on the intended application of the LLDPE resin. It is generally accepted that the poor optical properties of normal LLDPEs (haze  $>10$  and gloss  $<50$ ) severely limits their use in applications where film opticals are important. The films and extrudates of the invention with their improved optical properties (including, preferably, a gloss  $>70$ ) significantly broaden the application areas.

35 Films made of the polymeric component of the composition according to the invention exhibit dart impact properties as measured by ASTM D-1709, Method A. For example, such films exhibit superior dart drop over the films prepared with such previously-known catalysts. Such films exhibit Dart Drop Impact

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values as measured by ASTM D-1709 from 100 to 2000, preferably from 150 to 1500. The most preferred of such films exhibit densities of 0.911 to 0.922 g/cm<sup>3</sup> and dart drops of greater than 800, generally from 800 to 1500, and up to a measurement which  
 5 characterizes the product as unbreakable, e.g., a dart drop of 2000.

The above properties of the polymeric component of the composition according to the invention are for a 1 mil (25 micron) film made under a standard fabricating condition  
 10 outlined in the Examples, on a 0.75" (19 mm) Brabender extruder, 2.5" (64 mm) Brampton Film Extruder or a 3.5" (89 mm) Glouster Film Extruder. It is apparent to those familiar to the field that the film properties may be further modified by optimizing the fabricating conditions or by addition of LDPE or nucleating  
 15 agents.

The aforementioned properties of the polymeric component were determined by the following test methods:

20	Density	ASTM D-1505 - a plaque is made and conditioned for one hour at 100°C to approach equilibrium crystallinity. Measurement for density is then made in a density gradient column; reported as g/cm <sup>3</sup> .
25	Melt Index (MI), I <sub>2</sub>	ASTM D-1238 - Condition E Measured at 190°C - reported as grams per 10 minutes.
30	High Load Melt Index, I <sub>21</sub>	ASTM D-1238 - Condition F Measured at 10.5 times the weight used in (HLMI), the melt index test above.
35	Melt Flow Ratio (MFR) I <sub>2</sub>	I <sub>21</sub> /I <sub>2</sub>

The catalyst compositions employed to produce resins and films for the present invention may contain one transition metal



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in the form of a metallocene which has an activity of at least about 2,000 g polymer/g catalyst or about 1,000 kg polymer/g transition metal.

The catalysts preferably comprise a carrier, an aluminoxane  
5 and at least one metallocene.

The carrier material may be a solid, particulate, porous, inorganic or organic materials, but preferably inorganic material, such as an oxide of silicon and/or of aluminum. The carrier material may be used in the form of a dry powder having  
10 an average particle size of from about 1 micron to about 250 microns, preferably from about 10 microns to about 150 microns. If necessary, the treated carrier material may be sieved to ensure that the particles have an average particle size of preferably less than 150 microns. This is highly desirable in  
15 forming narrow molecular weight LLDPE, to reduce gels. The surface area of the carrier may be at least about 3 m<sup>2</sup>/g, and preferably at least about 50 m<sup>2</sup>/g up to about 350 m<sup>2</sup>/g. When the carrier is silica, it is heated to preferably about 100°C to about 850°C and most preferably at about 250°C. The carrier  
20 material preferably has at least some active hydroxyl (OH) groups to produce the catalyst composition of this invention.

In the most preferred embodiment, the carrier is silica which, prior to the use thereof in the first catalyst synthesis step, has been dehydrated by fluidizing it with nitrogen and  
25 heating at about 250°C for about 4 hours to achieve a surface hydroxyl group concentration of about 1.8 mmole/g. The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area = 250-350 m<sup>2</sup>/g; pore volume of 1.65 to 3.0 cm<sup>3</sup>/g), and it is a material marketed under the  
30 tradenames of PQ 988, Davison 952-1836, Davison 952 or Davison 955 by the Davison Chemical Division of W.R. Grace and Company. The silica is in the form of spherical particles, e.g., as obtained by a spray-drying process.

To form the catalysts, all catalyst precursor components  
35 can be dissolved with alumoxane and reacted with a carrier. The carrier material may be reacted with an aluminoxane solution, preferably methylalumoxane in a process described below. The

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class of alumoxanes comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula:  $R-(Al(R)-O)_n-AlR_2$  for oligomeric, linear alumoxanes; and  $(-Al(R)-O-)_m$  for oligomeric cyclic alumoxane wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a  $C_1-C_8$  alkyl group and preferably methyl. Methylalumoxane (MAO) is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 1000. MAO is typically kept in solution in toluene.

10 In a preferred embodiment, of alumoxane incorporation into the carrier, one of the controlling factors in the alumoxane incorporation into the carrier material during catalyst synthesis is the pore volume of the silica. In this preferred embodiment, the process of impregnating the carrier material is  
15 by infusion of the alumoxane solution, without forming a slurry of the carrier material, such as silica, in the alumoxane solution. The volume of the solution of the alumoxane is sufficient to fill the pores of the carrier material without forming a slurry in which the volume of the solution exceeds the  
20 pore volume of the silica; accordingly and preferably, the maximum volume of the alumoxane solution is and does not exceed the total pore volume of the carrier material sample. That maximum volume of the alumoxane solution ensures that no slurry of silica is formed. Accordingly, if the pore volume of the  
25 carrier material is  $1.65 \text{ cm}^3/\text{g}$ , then the volume of alumoxane will be equal to or less than  $1.65 \text{ cm}^3/\text{g}$  of carrier material. As a result of this proviso, the impregnated carrier material will appear dry immediately following impregnation although the pores of the carrier will be filled with inter alia solvent.

30 Solvent may be removed from the alumoxane impregnated pores of the carrier material by heating and/or under a positive pressure induced by an inert gas, such as nitrogen. If employed, the conditions in this step are controlled to reduce, if not to eliminate, agglomeration of impregnated carrier  
35 particles and/or crosslinking of the aluminosilicate. In this step, solvent can be removed by evaporation effected at relatively low elevated temperatures of above about  $40^\circ\text{C}$  and below about  $50^\circ\text{C}$ .

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Although solvent can be removed by evaporation at relatively higher temperatures than that defined by the range above 40°C and below about 50°C, very short heating times schedules must be employed.

5 In a preferred embodiment, the metallocene is added to the solution of the aluminosilane prior to reacting the carrier with the solution. Again the maximum volume of the aluminosilane solution also including the metallocene is the total pore volume of the carrier material sample. The mole ratio of aluminosilane  
10 provided aluminum, expressed as Al, to metallocene metal expressed as M (e.g. Zr), ranges from 50 to 500, preferably 75 to 300, and most preferably 100 to 200. An added advantage of the present invention is that this Al:Zr ratio can be directly controlled. In a preferred embodiment the aluminosilane and  
15 metallocene compound are mixed together at a temperature of about 20 to 80°C, for 0.1 to 6.0 hours, prior to reaction with the carrier. The solvent for the metallocene and aluminosilane can be appropriate solvents, such as aromatic hydrocarbons, halogenated hydrocarbon or halogenated aromatic hydrocarbons,  
20 preferably toluene.

The metallocene compound may have the formula  $Cp_mMA_nB_p$  in which Cp is an unsubstituted or substituted cyclopentadienyl group, M is zirconium or hafnium and A and B belong to the group including a halogen atom, hydrogen or an alkyl group. In the  
25 above formula of the metallocene compound, the preferred transition metal atom M is zirconium. In the above formula of the metallocene compound, the Cp group is an unsubstituted, a mono- or a polysubstituted cyclopentadienyl group. The substituents on the cyclopentadienyl group are preferably  
30 straight-chain or branched  $C_1-C_6$  alkyl groups. The cyclopentadienyl group can be also a part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when  
35 m in the above formula of the metallocene compound is equal to 2, the cyclopentadienyl groups can be also bridged by polymethylene or dialkylsilane groups, such as  $-CH_2-$ ,  $-CH_2-CH_2-$ ,

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-CR'R"- and -CR'R"-CR'R"- where R' and R" are short alkyl groups or hydrogen, -Si(CH<sub>3</sub>)<sub>2</sub>-, Si(CH<sub>3</sub>)<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-Si(CH<sub>3</sub>)<sub>2</sub>- and similar bridge groups. If the A and B substituents in the above formula of the metallocene compound are halogen atoms, they belong to  
5 the group of fluorine, chlorine, bromine or iodine. If the substituents A and B in the above formula of the metallocene compound are alkyl or aromatic groups, they are preferably straight-chain or branched C<sub>1</sub>-C<sub>8</sub> alkyl groups, such as methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, n-pentyl, n-hexyl  
10 or n-octyl.

Suitable metallocene compounds include bis(n-butylcyclopentadienyl)metal dihalides, bis(n-butylcyclopentadienyl)metal hydridohalides, bis(n-butylcyclopentadienyl)metal monoalkyl monohalides, bis(n-  
15 butylcyclopentadienyl)metal dialkyls and bis(indenyl)metal dihalides wherein the metal is titanium, zirconium or hafnium, halide groups are preferably chlorine and the alkyl groups are C<sub>1</sub>-C<sub>6</sub> alkyls. Illustrative, but non-limiting examples of metallocenes include bis(n-butylcyclopentadienyl)zirconium  
20 dichloride, bis(n-butylcyclopentadienyl)hafnium dichloride, bis(n-butylcyclopentadienyl)zirconium dimethyl, bis(n-butylcyclopentadienyl)hafnium dimethyl, bis(n-butylcyclopentadienyl)zirconium hydrido-chloride, bis(n-butylcyclopentadienyl)hafnium hydrido-chloride,  
25 bis(pentamethylcyclopentadienyl)zirconium dichloride, bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(methylcyclopentadienyl)zirconium dichloride, bis(iso-butylcyclopentadienyl) zirconium dichloride, bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-  
30 indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-tetrahydro-1-indenyl)] zirconium dichloride. The metallocene compounds utilized within the embodiment of this art can be used as crystalline solids, as solutions in aromatic hydrocarbons or in a supported form.

35 The catalyst comprising a metallocene compound and an aluminoxane in particulate form can be fed to a fluid bed reactor for gas phase polymerizations and copolymerizations of

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ethylene and higher alpha olefins or to a slurry reactor.

To ensure that sintering will not occur, operating temperatures below the sintering temperature are desired. For the production of ethylene copolymers in the process of the present invention an operating temperature of about 60° to 110°C is preferred, and a temperature of about 70° to 90°C is most preferred.

The fluid bed reactor may be operated at pressures of about 150 to 350 psi (1 to 2.4 MPa), with operation at the higher pressures in such ranges favoring heat transfer since an increase in pressure increases the unit volume heat capacity of the gas.

For film production, the products may contain any of various additives conventionally added to polymer compositions such as lubricants, microtalc, stabilizer, antioxidants, compatibilizers, pigments, etc. These reagents can be employed to stabilize the products against oxidation. For example, additive packages comprising 400-1200 ppm hindered phenol(s); 700-2000 ppm phosphites; 250 to 1000 ppm antistats and 250-1000 ppm stearates, for addition to the resin powders, can be used for pelletization. The pelletized polymers can be added directly to a conventional LLDPE blown film extruder, e.g., a Sterling extruder, to produce films having a thickness, for example of about 0.5 to 5 mils (13 to 130 micron).

The following Examples further illustrate the invention.

#### EXAMPLES

The metallocene catalyst described below was used in the pilot plant fluid bed 13 inch (0.33m) ID reactor with bed volume of 4.0 ft<sup>3</sup> (0.11 m<sup>3</sup>) for making the samples used in this work. Polymerization were carried out typically at 77.5 C and 170 to 200 psi (1.2 to 1.4 MPa) of ethylene. Hexene to ethylene gas ratio was varied from 0.009 to 0.025 to adjust the density. Isopentane partial from 0 to 50 psi (0 to 344 KPa) and oxygen addback level between 0.0 and 0.2 ppm or carbon dioxide addback of 0-10 ppm were used in order to achieve the desired melt index. The fluidized gas velocity is 1 to 2 ft/s (0.3 to 0.6

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m/s).

The reactor operability was good. The resin settled bulk density in all cases was between 31 to 34 lb/ft<sup>3</sup> (497 to 545 kg/m<sup>3</sup>) and the fines (defined as particle smaller than 120 Mesh) level is below 3%.

The resins used in these examples were listed in Table I. The additives, including 1000 PPM Irganox 1076, 2000 ppm Irgafos 168, 5000 ppm AS990, 500 ppm ZnSt and 0.2% Millad 3940, were incorporated into the resin by melt compounding using Brabender Extruder at 205 C. The Millad 3940 is bis(dimethylbenzylidene) sorbitol. The crystallization characteristics were measured using Differential Scanning Calorimeter (DSC-2 from Perkin - Elmer). The influences of Sorbitol derivatives on resin crystallization characteristics are presented in Table II. It has clearly demonstrated that the sorbitol derivative (Millad 3940 from Milliken) can act as a nucleating agent to raise the crystallization temperatures ( $T_c$ ) and reduce the half time for crystallization ( $t_{1/2}$ ) of PE resins markedly.

#### 20 Blown Film Results

The films were blown through a 3/4" (19 mm) Brabender extruder with a 1" (25 mm) annular die at a melt temperature of 210°. The optical properties of the 1.5 mil (38 micron) films prepared in this manner are presented, along with data for control PE films containing no Millad 3940, in Table I. The data clearly illustrate the marked improvement in clarity by the incorporation of small amounts of Millad 3940 into PE films.

Table 1

30	Sample	% Millad 3940	I <sub>2</sub>	Density(g/cm <sup>3</sup> )	% Haze
	1	0.0	0.94	0.924	12
	1	0.2	0.93	0.925	2.6
	2	0.0	0.94	0.928	11
	2	0.2	0.94	0.929	3.2
35	3	0.0	1.1	0.918	10.6
	3	0.2	1.1	0.918	2.1

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Table II

Sample	% Millad 3940	T <sub>m</sub> (°C)	T <sub>c</sub> (°C)	t <sub>1/2</sub> (s)
1	0.0	117	104	192
1	0.2	117	106	too fast to measure

5

The following examples relate to the manufacture of the polymeric component of the composition according to the invention, which comprises a narrow molecular weight distribution polymers and copolymers.

10 Example 1 [of WO-9414855]

Raw materials used in catalyst preparation included 505 g of Davison 952-1836 silica, 698 g of methylaluminoxane in toluene solution

15

(30 wt.% MAO), 7.148 g of bis(n-butylcyclopentadienyl) zirconium dichloride.

The steps of the catalyst preparation are set forth below:

20

1. Dehydrate the 955 silica at 250°C for 4 hours using air to purge. Then purge with nitrogen on cooling.
2. Transfer the silica to a mix-vessel.
3. Add 7.148 g of bis(n-butylcyclopentadienyl) zirconium dichloride and 698 g of methylaluminoxane to a bottle.

25

4. Agitate the catalyst solution in the bottle until the metallocene dissolves in the MAO solution.
5. Transfer the MAO and metallocene solution into the mix-vessel containing the dehydrated 955 silica slowly while agitating the silica bed vigorously to make sure that the catalyst solution is well dispersed into the silica bed.

30

6. After the addition, continue to agitate the catalyst for 0.5 hours.
7. Start drying the catalyst by purging with nitrogen for 5 hours at 45°C.

35

8. Sieve the catalyst to remove particles larger than 150 micron.

9. The catalyst has the following analysis:

Al = 10 wt.%

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Zr = 0.2 wt.%

Example 2 [of Serial No. WO-9414855]

To produce a polymer for low density film, 0.918 g/cm<sup>3</sup>, 1 MI, 17 MFR, in a fluid bed gas phase reactor the following 5 process conditions were employed.

	Fluidization velocity	1.7 ft/s (0.43 m/s)
	Residence time	2.5 hours
	Temperature	77.5 °C
	Ethylene	180 psi (1.2 MPa)
10	Hexene	3.6 psi (25 KPa)
	Isopentane	50 psi (345 KPa)
	Carbon dioxide	1.1 ppm
	Ash	200 to 250 ppm

The catalyst was that of Example 1.

15 Example 3 [of WO-9414855]

To produce a polymer for cast film of 0.918 g/cm<sup>3</sup> density, 2.5 MI, 16 MFR, the following process conditions were employed:

	Fluidization velocity	1.7 ft/s (0.43 m/s)
	Residence time	2.5 hours
20	Temperature	77.5 °C
	Ethylene	180 psi (1.2 MPa)
	Hexene	3.6 psi (25 KPa)
	Isopentane	38 psi (262 KPa)
	Ash	100 ppm

25 The catalyst was that of Example 1.

## 1. Resin Characteristics

When compared to a standard ethylene-hexene copolymer prepared with commercial Ziegler catalyst, the metallocene of Example 1 produced resins via the gas phase process which 30 exhibit the following characteristics: (1) narrower molecular weight distribution (2) more uniform short chain branching distribution, (3) lower melting point (4) lower extractables, and (5) lower haze.

An example of the key resin characteristics of a 1.0 I<sub>2</sub>, 35 0.918 g/cm<sup>3</sup> density resin is shown in Table III:



- 15 -

Table III

## LLDPE R sin Characteristics

1.0 I<sub>2</sub>, 0.918 g/cm<sup>3</sup> density

5 Property	Commercial Ziegler Metallocene (of Ex. 1)	
M <sub>w</sub> /M <sub>n</sub>	4.5	2.6
MFR	28	18
Melting point, °C	125	115

## 10 2. End-use property

These metallocene LLDPE resins can be processed readily on commercial equipment without modification. They also offer superior properties compared to those resins produced using commercial Ziegler/Natta catalysts. An example is given in

## 15 Table IV:

Table IV

## LLDPE Film Property Comparison

1.0 I<sub>2</sub>, 0.918 g/cm<sup>3</sup> density

2:1 BUR, 250 lb/hr (113 Kg/hr)

20

Property	Commercial Ziegler Metallocene (of Ex. 1)	
Melt Pressure, psi	5000	5500
(Melt Pressure MPa	34	38)
Bubble Stability	Very good	Very good
25 MD Modulus, 104 psi	2.8	2.5
(717 KPa)		
Dart Drop, g	180-450	>800
MD Tear, g/mil	350-450	370
(MD Tear, g/micron)	13.8-17.7	14.6)
30 Extractables, wt. %	2.5	0.6
Haze, %	10-18	5-7
Tensile Yield (x 103psi)	1.7	2.0
(x 710 KPa)		
Yield Elongation %	24	71

35

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Claims

1. A composition comprising a blend of:
  - (i) 99.95 to 98.5 weight percent of an ethylene polymer or an ethylene copolymer; and
  - 5 (ii) 0.05 to 1.5 weight percent of sorbitol or a sorbitol derivative;wherein the ethylene polymer or copolymer exhibits a MFR ( $I_{21}/I_2$ ) of 15 to less than 30,  $M_w/M_n$  of 2.5 to 3.5 and a haze value of greater than 7.
- 10 2. A composition according to Claim 1, wherein the sorbitol derivative is an ether or an ester of sorbitol.
3. A composition according to Claim 2, wherein the sorbitol  
15 derivative has an empirical formula  $H_8[(COH)_n[(CO)_2X]_m]$  in which  $m$  is 0, 1, 2 or 3,  $n$  is in the range 0 to 6, and  $2m+n$  is equal to 6; and wherein  $X$  is selected from the group consisting of:
  - (1) alkyl or aryl of 1 to 8 carbon atoms;
  - (2)  $-C(O)R$ , wherein  $R$  is alkyl or aryl of 1 to 8 carbon  
20 atoms;
  - (3) admixtures of (1) and (2).
4. A composition according to Claim 3, wherein  $m$  is in the range 1 to 3.
- 25 5. A composition according to Claim 3, wherein  $m$  is 2 or 3.
6. A composition according to Claim 3, wherein  $n$  is in the range 1 to 6.
- 30 7. A composition according to Claim 3, wherein the sorbitol derivative is bis(dimethylbenzylidene) sorbitol.
8. A composition according to Claim 3, wherein the sorbitol  
35 derivative is dimethyl-dibenzylidene sorbitol.
9. A composition according to claim 1, 2, or 3, wherein the

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ethylene copolymer comprises linear low density polyethylene which is a copolymer of ethylene and at least one alpha olefin containing 3 to 10 carbon atoms.

5 10. A composition according to Claim 9, wherein the alpha olefin is 1-hexene.

11. A composition according to Claim 1, 2 or 3, which comprises a film exhibiting a haze value measured by ASTM D-1003 of less  
10 than 7.

12. A composition according to Claim 1, 2 or 3, which comprises an extrudate exhibiting a haze value measured by ASTM D-1003 of less than 7.

## INTERNATIONAL SEARCH REPORT

 International application No.  
PCT/US94/12813

<b>A. CLASSIFICATION OF SUBJECT MATTER</b> IPC(6) : Please See Extra Sheet. US CL : Please See Extra Sheet. According to International Patent Classification (IPC) or to both national classification and IPC																				
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) U.S. : Please See Extra Sheet. Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)																				
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>																				
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.																		
Y	US, A, 4,808,561 (WELBORN, JR.) 28 February 1989, col. 2, lines 32-44, col. 8, line 35 to col. 9, line 25, col. 10, lines 49-53, and col. 11, line 20 to col. 13, line 60.	1-12																		
Y	US, A, 4,937,301 (CHANG) 26 June 1990, col. 9, line 1 to col. 11, line 11.	1-12																		
Y	US, A, 5,026,797 (TAKAHASHI) 25 June 1991, col. 6, line 35 to col. 9, line 14.	1-12																		
Y	US, A, 5,057,475 (CANICH ET AL.) 15 October 1991, col. 16, line 58 to col. 23, line 25.	1-12																		
Y	US, A, 5,210,167 (FIRDAUS ET AL.) 11 May 1993, col. 1, line 28 to col. 2, line 2.	1-12																		
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.																				
<table border="0"> <tr> <td colspan="2">           * Special categories of cited documents:         </td> <td></td> </tr> <tr> <td>*A*</td> <td>document defining the general state of the art which is not considered to be part of particular relevance</td> <td>*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</td> </tr> <tr> <td>*E*</td> <td>earlier document published on or after the international filing date</td> <td>*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</td> </tr> <tr> <td>*L*</td> <td>document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</td> <td>*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</td> </tr> <tr> <td>*O*</td> <td>document referring to an oral disclosure, use, exhibition or other means</td> <td></td> </tr> <tr> <td>*P*</td> <td>document published prior to the international filing date but later than the priority date claimed</td> <td>*A* document member of the same patent family</td> </tr> </table>			* Special categories of cited documents:			*A*	document defining the general state of the art which is not considered to be part of particular relevance	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	*E*	earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	*L*	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art	*O*	document referring to an oral disclosure, use, exhibition or other means		*P*	document published prior to the international filing date but later than the priority date claimed	*A* document member of the same patent family
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*E*	earlier document published on or after the international filing date	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone																		
*L*	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art																		
*O*	document referring to an oral disclosure, use, exhibition or other means																			
*P*	document published prior to the international filing date but later than the priority date claimed	*A* document member of the same patent family																		
Date of the actual completion of the international search 16 DECEMBER 1994		Date of mailing of the international search report 12 JAN 1995																		
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. (703) 305-3230		Authorized officer ROMULO H. DELMENDO Telephone No. (703) 308-2351																		

## INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/12813

## C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y, P	US, A, 5,272,236 (LAI ET AL.) 21 December 1993, col. 2, lines 22-50 and col. 14, lines 8-47.	1-12
Y, P	US, A, 5,296,580 (MATSUNAGA ET AL.) 22 March 1994, col. 1, line 55 to col. 2, line 11.	1-12
Y	US, A, 5,015,684 (KOBAYASHI ET AL.) 14 May 1991, col. 2, line 63 to col. 3, line 50 and col. 5, line 55 to col. 6, line 12.	1-12
Y	US, A, 5,049,605 (REKERS) 17 September, 1991, col. 3, lines 30-55 and col. 5, lines 3-26.	1-12

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US94/12813

**A. CLASSIFICATION OF SUBJECT MATTER:**  
IPC (6):

C08K 5/05, 5/06

**A. CLASSIFICATION OF SUBJECT MATTER:**  
US CL :

524/108, 387, 381, 570, 579, 585

**B. FIELDS SEARCHED**

Minimum documentation searched  
Classification System: U.S.

524/108, 387, 381, 570, 579, 585